

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 540 009 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **92118554.2**(51) Int. Cl.⁵: **C07D 301/06, C07D 303/02**(22) Date of filing: **29.10.92**

(30) Priority: **30.10.91 JP 284651/91**
11.03.92 JP 52438/92
11.03.92 JP 52441/92

(43) Date of publication of application:
05.05.93 Bulletin 93/18

(84) Designated Contracting States:
BE CH DE FR GB IT LI NL

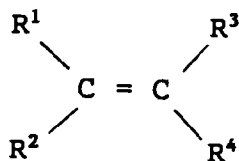
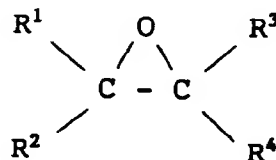
(71) Applicant: **SUMITOMO CHEMICAL COMPANY, LIMITED**
5-33, Kitahama 4-chome Chuo-ku
Osaka(JP)

(72) Inventor: **Murahashi, Shun-Ichi**
3-29, Asahigaoka-1-chome
Ikeda-shi(JP)
Inventor: **Oda, Yoshiaki**
10-4-449, Sonehlgashinocho-2-chome
Toyonaka-shi(JP)

(74) Representative: **Vossius & Partner**
Siebertstrasse 4 P.O. Box 86 07 67
W-8000 München 86 (DE)

(54) **Process for producing epoxides.**

(57) A process for producing an epoxide represented by the formula (2) which comprises reacting an olefin represented by the formula (1) with oxygen in the presence of an aldehyde and in the presence or absence of a proton source by using no catalyst or using an iron-containing or copper-containing catalyst.

**Formula (1)****Formula (2)****EP 0 540 009 A1**

The present invention relates to a process for producing an epoxide represented by the formula (2) shown later.

The epoxide mentioned above is important as an intermediate in producing a wide variety of products, including perfumes, pharmaceuticals, agricultural chemicals, liquid crystals and resins.

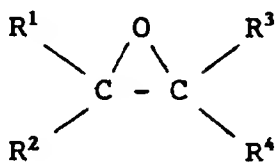
It is well known to convert an olefin to the corresponding epoxide by using peracids such as peracetic acid, m-chloroperbenzoic acid, and the like (Some Modern Methods of Organic Synthesis, 3rd ed., P. 370-373). However, since peracids are highly sensitive to shock and are explosive, this method cannot be said to be an advantageous process from the industrial point of view.

To overcome such difficulty, processes have already been developed which comprise oxidizing an olefin with oxygen in the presence of an aldehyde by using a catalyst containing a soluble praseodymium compound (Japanese Patent Application KOKAI No. 59-231077) or a soluble nickel catalyst (Chem. Lett., 1991, 1). However, since these processes use a homogeneous catalyst, they require complicated operations in the separation of the epoxide, the intended product, from the catalyst and in the recovery of the catalyst, and further, when the catalyst is not recovered, the processes will produce a waste water with a high content of undesirable substances. Thus, they are not fully satisfactory as industrial processes.

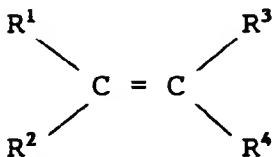
The object of the present invention is to provide an advantageous process for producing epoxides by oxidizing olefins with oxygen in the presence of an aldehyde which uses no catalyst or uses a catalyst that is easily available and recoverable and that will bring little of undesirable substances into the waste water.

This object has been attained by the present invention.

Thus, according to the present invention, there is provided a process for producing an epoxide represented by the formula (2)



wherein R^1 , R^2 , R^3 and R^4 may be the same or different and each denotes a hydrogen atom, $(\text{C}_1 - \text{C}_{20})$ alkyl group; alkyl group substituted with a halogen, hydroxy, alkoxy, phenoxy, acyloxy, acyl, alkoxycarbonyl or phenoxycarbonyl; phenyl group, phenyl group substituted with a halogen, alkyl, alkoxy, phenoxy, acyloxy, acyl, alkoxycarbonyl or phenoxycarbonyl; phenylalkyl group, phenylalkyl group substituted with a halogen, alkyl, alkoxy, phenoxy, acyloxy, acyl, alkoxycarbonyl or phenoxycarbonyl; acyl group, alkoxycarbonyl group or phenoxycarbonyl group; provided that R^1 and R^2 or R^1 and R^3 may combine with each other to form a ring, or R^1 , R^2 and R^3 may combine altogether to form a condensed ring, which comprises reacting an olefin represented by the formula (1)



wherein R^1 , R^2 , R^3 and R^4 are the same as defined above, with oxygen in the presence of an aldehyde, preferably in the presence or absence of a proton source and in the presence or absence of an iron-containing catalyst or a copper-containing catalyst.

Generally, the terms alkyl and acyl, alone or as part of another group, comprise residues having up to 20, preferably up to 10, more preferably 1 to 6 carbon atoms.

Examples of the olefin represented by the formula (1) used in the present invention include ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, pentadecene, eicocene, methylbutene, methylpentene, methylhexene, methylheptene, methyldecene, methyltetradecene, dimethylbutene, dimethylpentene, dimethylhexene, dimethylheptene, dimethyldecene, trimethylnonene, ethylpentene, ethylhexene, ethylheptene, n-propylnonene, tetramethylnonene, tetramethyldecene, ethyl-

n-propyldecene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclododecene, methylcyclopentene, methylcyclohexene, ethylcyclohexene, ethylcyclooctene, dimethylcyclohexene, norbornene, pinene, allyl chloride, allyl bromide, crotyl chloride, crotyl bromide, 1,4-dichlorobutene, pentenol, cyclohexenol, terpineol, methyl pentenyl ether, cyclohexenyl ethyl ether, cyclohexenyl phenyl ether, pentenyl acetate, cyclohexenyl acetate, pentenone, hexenone, heptenone, methyl hexenoate, ethyl oleate, phenyl hexenoate, phenyl oleate, styrene, methylstyrene, ethylstyrene, stilbene, p-chlorostyrene, m-chlorostyrene, p-methylstyrene, p-ethylstyrene, p-methoxystyrene, p-ethoxystyrene, methylisoeugenol, m-phenoxy styrene, p-acetoxystyrene, p-acetylstyrene, p-methoxycarbonylstyrene, p-phenoxy carbonylstyrene, phenylbutene, phenylpentene, phenylhexene, phenyloctene, p-chlorophenylbutene, m-chlorophenylbutene, p-methylphenylbutene, p-ethylphenylbutene, p-methoxyphenylbutene, p-ethoxyphenylbutene, m-phenoxyphenylbutene, p-acetoxyphe nylbutene, p-acetylphenylbutene, p-methoxycarbonylphenylbutene, p-phenoxy carbonylphenylbutene, cyclohexenone, methyl cinnamate, methyl p-methoxycinnamate, phenyl cinnamate, cholesterol, and cholesteryl acetate. The positions of the substituents in the olefins are optional, and the olefins include, if any, the geometric isomers.

The epoxide which is the intended compound of the present invention can be obtained as the epoxide represented by the formula (2) by using the above-mentioned olefin. Examples of the epoxide include ethylene oxide, propylene oxide, butene oxide, pentene oxide, hexene oxide, heptene oxide, octene oxide, nonene oxide, decene oxide, undecene oxide, dodecene oxide, pentadecene oxide, eicocene oxide, methylbutene oxide, methylpentene oxide, methylhexene oxide, methylheptene oxide, methyldecene oxide, methyltetradecene oxide, dimethylbutene oxide, dimethylpentene oxide, dimethylhexene oxide, dimethylheptene oxide, dimethyldecene oxide, trimethylnonene oxide, ethylpentene oxide, ethylhexene oxide, ethylheptene oxide, n-propylnonene oxide, tetramethylnonene oxide, tetramethyldecene oxide, ethyl-n-propyldecene oxide, cyclopentene oxide, cyclohexene oxide, cycloheptene oxide, cyclooctene oxide, cyclododecene oxide, methylcyclopentene oxide, methylcyclohexene oxide, ethylcyclohexene oxide, ethylcyclooctene oxide, dimethylcyclohexene oxide, norbornene oxide, pinene oxide, epichlorohydrin, epibromohydrin, 1-chloro-2,3-epoxybutane, 1-bromo-2,3-epoxybutane, 1,4-dichloro-2,3-epoxybutane, epoxypentanol, epoxycyclohexanol, terpineol oxide, epoxypentyl methyl ether, epoxycyclohexyl ethyl ether, epoxycyclohexyl phenyl ether, epoxypentyl acetate, epoxycyclohexyl acetate, epoxypentanone, epoxyhexanone, epoxyheptanone, methyl epoxyhexanoate, ethyl epoxyoctadecanoate, phenyl epoxyhexanoate, phenyl epoxyoctadecanoate, styrene oxide, methylstyrene oxide, ethylstyrene oxide, stilbene oxide, p-chlorostyrene oxide, m-chlorostyrene oxide, p-methylstyrene oxide, p-ethylstyrene oxide, p-methoxystyrene oxide, p-ethoxystyrene oxide, 1-(3',4'-dimethoxyphenyl)-1,2-epoxypropane, p-acetoxystyrene oxide, p-acetylstyrene oxide, p-methoxycarbonylstyrene oxide, p-phenoxy carbonylstyrene oxide, phenylbutene oxide, phenylpentene oxide, phenylhexene oxide, phenyloctene oxide, p-chlorophenylbutene oxide, m-chlorophenylbutene oxide, p-methylphenylbutene oxide, p-ethylphenylbutene oxide, p-methoxyphenylbutene oxide, p-ethoxyphenylbutene oxide, m-phenoxyphenylbutene oxide, p-acetoxyphe nylbutene oxide, p-acetylphenylbutene oxide, p-methoxycarbonylphenylbutene oxide, p-phenoxy carbonylphenylbutene oxide, epoxycyclohexanone, methyl 3-phenylglycidate, methyl 3-(4-methoxyphenyl)glycidate, phenyl 3-phenylglycidate, 5,6-epoxy-3-cholestanol and 5,6-epoxy-3-cholestanyl acetate.

Examples of the iron-containing catalyst include Fe, Fe(CO)₅, Fe(CO)₉, Fe(CO)₁₂, FeO, FeCl₂·nH₂O, FeBr₂·nH₂O, FeSO₄·nH₂O, FeCl₃·nH₂O, Fe₂(SO₄)₃·nH₂O, Fe(NO₃)₃·nH₂O, Fe(OAc)₃, Fe₂O₃ and Fe₃O₄, preferably Fe, FeCl₂·nH₂O, FeSO₄·nH₂O, FeCl₃·nH₂O, Fe(OAc)₃ and Fe₂O₃, more preferably Fe and Fe₂O₃. Examples of the copper-containing catalyst include Cu, CuCl, CuCl₂·nH₂O, CuBr, CuBr₂, CuI, CuF₂, CuSO₄·nH₂O, Cu(NO₃)₃·nH₂O, Cu(ClO₄)₂·nH₂O, Cu(OH)₂, Cu(OCH₃)₂, Cu₃(PO₄)₂·nH₂O, Cu₂O, CuO and Cu(OAc)₂·nH₂O, preferably Cu, CuCl, Cu(OAc)₂·nH₂O, Cu(OH)₂, Cu(OCH₃)₂, Cu₂O and CuO, more preferably Cu, Cu(OH)₂, Cu₂O and CuO. In the above examples of the catalysts, n is normally an integer of 0 to 7. These catalysts may also be used as a mixture thereof, or may also be used after supported on heteropolyacids, silica gel, carbon powders, polymers, and other suitable carriers. The amount of the catalyst to be used is not particularly limited but is usually in the range of 0.01-120% by mole, preferably 0.1-10% by mole, relative to the olefin.

Examples of the aldehyde include formaldehyde, acetaldehyde, propionaldehyde, butanal, pentanal, hexanal, heptanal, decanal, 2-methylpropanal, 2-methylbutanal, cyclohexanecarboxaldehyde, isovaleraldehyde, benzaldehyde, m-chlorobenzaldehyde, p-chlorobenzaldehyde, p-tolualdehyde, p-anisaldehyde, and pivalaldehyde. When the oxidation is performed in the absence of a catalyst, 2-methylpropanal, 2-methylbutanal, isovaleraldehyde, and pivalaldehyde are preferably used. The amount of the aldehyde to be used is not particularly limited but is usually in the range of 1-30 moles, preferably 1-10 moles, per mole of the olefin.

The addition of a proton source is particularly effective when the transition metal catalyst used is a simple substance. Examples of the proton source include formic acid, acetic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, trifluoroacetic acid, propanoic acid, butyric acid, heptanoic acid, decanoic acid, benzoic acid, p-toluenesulfonic acid, hydrochloric acid, hydrogen
 5 bromide, sulfuric acid, nitric acid and water, preferably acetic acid and benzoic acid. The amount of the proton source to be used is not particularly limited, but is usually in the range of 1 – 100 moles per mole of the iron – containing or copper – containing catalyst. When the iron – containing or copper – containing catalyst contains water, however, the use of the proton source is not necessary.

In the process of the present invention, the reaction may also be performed in a solvent. Examples of
 10 the solvent which may be used include halogenated hydrocarbons such as dichloromethane, chloroform and ethylene dichloride, esters such as ethyl acetate, nitriles such as acetonitrile and aromatic hydrocarbons such as benzene, toluene, xylene, monochlorobenzene and dichlorobenzene.

The oxygen used in the present invention may be, besides oxygen, also air. The method of supplying the oxygen is not particularly restricted, and the reaction is generally conducted by blowing oxygen into the
 15 system, or under oxygen atmosphere, or supplying oxygen by other suitable means.

The method of feeding the olefin is not particularly limited but, when Fe_2O_3 is used, the olefin is preferably fed last.

The reaction temperature is usually in the range from 0 °C to the reflux temperature of the reaction mixture, preferably in the range from 20 °C to 80 °C.

20 The reaction time is not particularly limited. The reaction mixture may be analyzed by means of GC (gas chromatography) or the like, and the time at which the conversion to the intended epoxide levels off may be taken as the end point of the reaction. The reaction times is usually in the range from 1 to 48 hours.

In the present reaction, the aldehyde used is converted into the corresponding carboxylic acid and can be easily separated from the intended product.

25 After completion of the reaction, the intended epoxide can be obtained, for example, by recovering the catalyst by filtration and then subjecting the filtrate to washing with aqueous sodium hydrogencarbonate solution, then concentration and, if necessary, further operations such as rectification.

The process of the present invention is an industrially excellent one which can produce a corresponding epoxide from an olefin through a reaction with oxygen in the presence of an aldehyde, in the presence or
 30 absence of a proton source, and in the absence of a catalyst or by using an iron – containing or copper – containing catalyst which is easily available and recoverable and which brings little of undesirable substances into the waste water.

The present invention will be described in more detail below with reference to Examples, but it is in no way limited thereto.

35 Example 1

A mixture of 164 mg of cyclohexene, 433 mg of 2-methylpropanal and 10 ml of dichloromethane was stirred overnight under an oxygen atmosphere at 25 °C. Analysis of the reaction mixture by GC showed that
 40 cyclohexene oxide had been formed in 90% yield.

Example 2

45 A mixture of 272 mg of α – pinene, 517 mg of isovaleraldehyde and 10 ml of dichloromethane was stirred overnight under an oxygen atmosphere at 25 °C. Analysis of the reaction mixture by GC showed that α – pinene oxide had been formed in 86% yield.

Example 3

50 A mixture of 164 mg of cyclohexene, 517 mg of 2-methylbutanal and 10 ml of dichloromethane was stirred overnight under an oxygen atmosphere at 25 °C. Analysis of the reaction mixture by GC showed that cyclohexene oxide had been formed in 88% yield.

Examples 4 – 6

55 Mixtures of 2 mmoles of an olefin, 517 mg of pivalaldehyde and 10 ml of dichloromethane were stirred overnight under an oxygen atmosphere at 25 °C. Analysis of the reaction mixtures by GC gave the results shown in Table 1.

Table 1

Example No.	Olefin	Product	Yield* ¹⁾ (%)
4	1 – Decene	1 – Decene oxide	65
5	trans – 5 – Decene	trans – 5 – Decene oxide	92
6	cis – Stilbene	cis – Stilbene oxide trans – Stilbene oxide	38 48

Note:

*1) Based on olefin

Examples 7 – 12

A solution of 914 mg of heptanal in 2 ml of dichloromethane was added dropwise over a period of 1 hour to respective mixtures of 164 mg of cyclohexene, 1% by mole (relative to cyclohexene) of a catalyst, 1.2 mg of acetic acid and 10 ml of dichloromethane under an oxygen atmosphere at 25 °C, and the resulting mixtures were stirred for further 15 hours at the same temperature. Analysis of the reaction mixtures by GC gave the results shown in Table 2.

Table 2

Example No.	Catalyst	Cyclohexene oxide yield* ¹⁾ (%)
7	Fe	71
8	FeCl ₂ • 4H ₂ O	6
9	FeSO ₄ • 7H ₂ O	18
10	FeCl ₃ • 6H ₂ O	8
11	Fe(OAc) ₃	30
12	Fe ₂ O ₃	10

Note:

*1) Based on cyclohexene

Examples 13 – 18

Mixtures of 281 mg of 1 – decene, 1% by mole (relative to 1 – decene) of a catalyst, 1.2 mg of acetic acid, 685 mg of heptanal and 10 ml of dichloromethane were stirred under an oxygen atmosphere at 25 °C for 17 hours. Analysis of the reaction mixtures gave the results shown in Table 3.

Table 3

Example No.	Catalyst	Conversion ^{*1)}	1 – Decene oxide yield ^{*2)} (%)
13	Fe	56	52(92)
14	FeCl ₂ • 4H ₂ O	11	5(49)
15	FeSO ₄ • 7H ₂ O	5	4(81)
16	FeO	6	5(84)
17	FeCl ₃ • 6H ₂ O	6	4(65)
18	Fe(OAc) ₃	9	7(82)

Note:

*1) Based on 1 – decene.

*2) Based on 1 – decene. Values in parenthesis are based on converted 1 – decene.

Examples 19 – 24

Mixtures of 281 mg of 1 – decene, 1.1 mg of Fe, 1.2 mg of acetic acid, 6 mmoles of an aldehyde and 10 ml of dichloromethane were stirred under an oxygen atmosphere at 25 °C for 17 hours. The reaction mixtures were analyzed by GC to obtain the results shown in Table 4.

Table 4

Example No.	Aldehyde	Conversion ^{*1)} (%)	1 – Decene oxide yield ^{*2)} (%)
19	Acetaldehyde	3	3(100)
20	Butanal	73	59(81)
21	2 – Methylpropanal	37	28(75)
22	Cyclohexanecarboxaldehyde	30	25(84)
23	Pivalaldehyde	44	32(73)
24	Benzaldehyde	16	12(77)

Note:

*1) Based on 1 – decene.

*2) Based on 1 – decene. Values in parenthesis are based on converted 1 – decene.

Examples 25 – 29

Mixtures of 281 mg of 1 – decene, 1.1 mg of Fe, 1% by mole (relative to 1 – decene) of an acid, 685 mg of heptanal and 10 ml of dichloromethane were stirred under an oxygen atmosphere at 25 °C for 17 hours. The reaction mixtures were analyzed by GC to obtain the results shown in Table 5.

Table 5

Example No.	Acid	Conversion ^{*1)} (%)	1 – Decene oxide yield ^{*2)} (%)
25	Benzoic acid	59	56(95)
26	Formic acid	56	51(91)
27	Heptanoic acid	58	53(91)
28	Trifluoroacetic acid	58	45(78)
29	p – toluenesulfonic acid	41	39(94)

Note:

*1) Based on 1 – decene.

*2) Based on 1 – decene. Values in parenthesis are based on converted 1 – decene.

Examples 30 – 32

Mixtures of 281 mg of 1 – decene, 1.1 mg of Fe, 2.4 mg of benzoic acid, 685 mg of heptanal and 10 ml of a solvent were stirred under an oxygen atmosphere at 25 °C for 17 hours. The reaction mixtures were analyzed by GC to obtain the results shown in Table 6.

Table 6

Example No.	Solvent	conversion ^{*1)} (%)	1 – Decene oxide yield ^{*2)} (%)
30	Acetonitrile	61	56(92)
31	Benzene	31	31(99)
32	Ethyl acetate	12	12(99)

Note:

*1) Based on 1 – decene.

*2) Based on 1 – decene. Values in parenthesis are based on converted 1 – decene.

Examples 33 – 34

Mixtures of 281 mg of 1 – decene, 1.1 mg of Fe, 2.4 mg of benzoic acid, heptanal and 10 ml of dichloromethane were stirred under an oxygen atmosphere at 25 °C for 17 hours. The reaction mixtures were analyzed by GC to obtain the results shown in Table 7.

Table 7

Example No.	Heptanal equivalent (relative to 1 – decene)	Conversion ^{*1)} (%)	1 – Decene oxide yield ^{*2)} (%)
33	2	38	37(98)
34	4	64	55(86)

Note:

*1) Based on 1 – decene.

*2) Based on 1 – decene. Values in parenthesis are based on converted 1 – decene.

Examples 35 - 37

Mixtures of 281 mg of 1-decene, Fe, 2.4 mg of benzoic acid, 685 mg of heptanal and 10 ml of dichloromethane were stirred under an oxygen atmosphere at 25 °C for 17 hours. The reaction mixtures were analyzed by GC to obtain the results shown in Table 8.

Table 8

Example No.	Fe equivalent (relative to 1-decene)	Conversion ^{*1)} (%)	1-Decene oxide yield ^{*2)} (%)
35	0.001	58	52 (89)
36	0.05	56	48 (85)
37	0.10	56	47 (83)

Note: *1) Based on 1-decene.

*2) Based on 1-decene. Values in parenthesis are based on converted 1-decene.

Examples 38 - 45

Mixtures of 2 mmoles of an olefin, 1.1 mg of Fe, 2.4 mg of benzoic acid, 685 mg of heptanal and 10 ml of dichloromethane were stirred under an oxygen atmosphere at 25 °C for 17 hours. The reaction mixtures were analyzed by GC to obtain the results shown in Table 9.

Table 9

Example No.	Olefin	Conversion ^{*1)} (%)	Product	Yield ^{*2)} (%)
38	Cyclohexene	100	Cyclohexene oxide	79(79)
39	trans - 5 - Decene	100	trans - 5 - Decene oxide	89(89)
40	cis - 5 - Decene	100	cis - 5 - Decene oxide trans - 5 - Decene oxide	56(56) 30(30)
41	1 - Methylcyclohexene	29	1 - Methylcyclohexene oxide	29(100)
42	α - Pinene	23	α - Pinene oxide	23(99)
43	trans - Stilbene	14	trans - Stilbene oxide	12(84)
44	cis - Stilbene	28	cis - Stilbene oxide trans - Stilbene oxide	5(16) 21(76)
45	2 - Cyclohexenol	100	2,3 - Epoxy - 1 - cyclohexanol	38(38)

Note:

*1) Based on olefin

*2) Based on olefin. Values in parenthesis are based on converted olefin.

Examples 46 – 50

Examples 38 – 45 were repeated except that 517 mg of pivalaldehyde was used in place of 685 mg of heptanal, to obtain the results shown in Table 10.

Table 10

Example No.	Olefin	Conversion ^{*1)} (%)	Product	Yield ^{*2)} (%)
46	1 – Methylcyclohexene	100	1 – Methylcyclohexene oxide	88(88)
47	α – Pinene	100	α – Pinene oxide	81(81)
48	trans – Stilbene	100	trans – Stilbene oxide	90(90)
49	cis – Stilbene	66	cis – Stilbene oxide trans – Stilbene oxide	9(13) 44(66)
50	Methyl p – methoxycinnamate	47	Methyl 3 – (4 – methoxyphenyl)glycidate	43(90)

Note:

*1) Based on olefin.

*2) Based on olefin. Values in parenthesis are based on converted olefin.

Examples 51 – 54

Mixtures of 272 mg of α – pinene, 1.1 mg of Fe, 2.4 mg of benzoic acid, 6 mmoles of an aldehyde and 10 ml of dichloromethane were stirred under an oxygen atmosphere at 25 °C for 17 hours. The reaction mixtures were analyzed by GC to obtain the results shown in Table 11.

Table 11

Example No.	Aldehyde	Conversion ^{*1)} (%)	α – Pinene oxide Yield ^{*2)} (%)
51	Butanal	11	11(98)
52	Isovaleraldehyde	42	33(79)
53	2 – Methylpropanal	91	72(79)
54	Benzaldehyde	12	11(98)

Note:

*1) Based on α – pinene.

*2) Based on α – pinene. Values in parenthesis are based on converted α – pinene.

Example 55

A solution of 1.83 g of heptanal in 4 ml of dichloromethane was added dropwise over a period of 1 hour to a mixture of 561 mg of trans – 5 – decene, 2.2 mg of Fe, 2.4 mg of acetic acid and 20 ml of dichloromethane under an oxygen atmosphere at 25 °C, and the resulting mixture was stirred for further 15 hours at the same temperature. The reaction mixture was analyzed by GC to obtain the following results.

Conversion : 87%

trans – 5 – Decene oxide yield :

84% (based on trans – 5 – decene)

97% (based on converted trans – 5 – decene)

cis – 5 – Decene oxide yield :

3% (based on trans – 5 – decene)

3% (based on converted trans – 5 – decene)

Examples 56 - 66

A mixture of 637 mg of benzaldehyde, 3.2 mg of Fe₂O₃ and 12 ml of benzene was stirred vigorously under an oxygen atmosphere at room temperature, and then 2 mmoles of an olefin was added thereto over a period of 0.5 hours. After completion of the addition, the mixture was stirred for further 17 hours at the same temperature. The reaction mixture was analyzed by GC to obtain the results shown in Table 12.

Table 12

Example No.	Olefin	Conversion* ¹⁾ (%)	Product	Yield* ²⁾ (%)
56	Cyclohexene	100	Cyclohexene oxide	97(97)
57	α -Pinene	100	α -Pinene oxide	90(90)
58	Styrene	100	Styrene oxide	85(85)
59	p-Chloro-styrene	100	p-Chloro-styrene oxide	81(81)
60	p-Methoxy-styrene	100	p-Methoxy-styrene oxide	89(89)
61	Crotyl bromide	96	1-Bromo-2,3-epoxybutane	96(100)
62	trans-1,4-Dichloro-2-butene	91	trans-1,4-Dichloro-2,3-epoxybutane	90(99)
63	Norbornene	100	Norbornene oxide	100(100)
64	α -Terpineol	100	α -Terpineol oxide	80(80)
65	Methyl-isoeugenol	98	1-(3,4-Dimethoxy-phenyl)-1,2-epoxy-propane	84(86)
66	Cholesteryl acetate	-	5,6-Epoxy-3-cholestanyl acetate	88* ³⁾

Note: *1) Based on olefin.

*2) Based on olefin. Values in parenthesis are based on converted olefin.

*3) Isolated yield

Examples 67 – 71

A solution of 897 mg of cyclohexanecarboxaldehyde in 2 ml of dichloromethane was added dropwise over a period of 2 hours to a mixture of 164 mg of cyclohexene, 3% by mole (relative to cyclohexene) of a catalyst, 1.2 mg of acetic acid and 10 ml of dichloromethane under an oxygen atmosphere at 25 °C, and the resulting mixture was stirred at the same temperature for further 15 hours. The reaction mixture was analyzed by GC to obtain the results shown in Table 13.

Table 13

Example No.	Catalyst	Cyclohexene oxide yield* ¹) (%)
67	Cu	80
68	Cu(OAc) ₂	85
69	CuCl	78
70	Cu ₂ O	82
71	CuO	75

Note:

*1) Based on cyclohexene.

Examples 72 – 75

Mixtures of 281 mg of 1-decene, 1% by mole (relative to 1-decene) of a catalyst, 637 mg of benzaldehyde and 12 ml of dichloromethane were stirred under an oxygen atmosphere at 25 °C for 17 hours. The reaction mixtures were analyzed by GC to obtain the results shown in Table 14.

Table 14

Example No.	Catalyst	Conversion* ¹) (%)	1 – Decene oxide yield* ²) (%)
72	Cu(OCH ₃) ₂	53	30(57)
73	Cu(OH) ₂	51	32(64)
74	Cu	42	26(60)
75	Cu(OAc) ₂	40	25(63)

Note:

*1) Based on 1 – decene.

*2) Based on 1 – decene. Values in parenthesis are based on converted 1 – decene.

Examples 76 – 82

Mixtures of 2 mmoles of an olefin, 1.0 mg of Cu(OH)₂, 673 mg of cyclohexanecarboxaldehyde and 12 ml of dichloromethane were stirred under an oxygen atmosphere for 17 hours. The reaction mixtures were analyzed by GC to obtain the results shown in Table 15.

Table 15

Example No.	Olefin	Conversion ^{*1)} (%)	Product	Yield ^{*2)} (%)
76	1 – Decene	51	1 – Decene oxide	27(83)
77	Cyclohexene	100	Cyclohexene oxide	79(79)
78	trans – 5 – Decene	83	trans – 5 – Decene oxide	80(96)
79	cis – 5 – Decene	96	cis – 5 – Decene oxide trans – 5 – Decene oxide	19(20) 63(66)
80	α – Pinene	100	α – Pinene oxide	84(84)
81	trans – Stilbene	93	trans – Stilbene oxide	76(82)
82	cis – Stilbene	81	cis – Stilbene oxide trans – Stilbene oxide	7(9) 57(70)

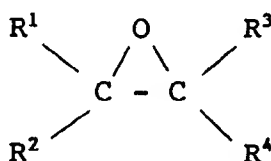
Note:

*1) Based on olefin.

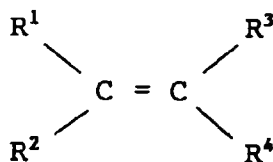
*2) Based on olefin. Values in parenthesis are based on converted olefin.

Claims

1. A process for producing an epoxide represented by the formula (2)



wherein R^1 , R^2 , R^3 and R^4 may be the same or different and each denotes a hydrogen atom, ($C_1 - C_{20}$)alkyl group, alkyl group substituted with a halogen, hydroxy, alkoxy, phenoxy, acyloxy, acyl, alkoxy carbonyl or phenoxy carbonyl; phenyl group, phenyl group substituted with a halogen, alkyl, alkoxy, phenoxy, acyloxy, acyl, alkoxy carbonyl or phenoxy carbonyl; phenylalkyl group, phenylalkyl group substituted with a halogen, alkyl, alkoxy, phenoxy, acyloxy, acyl, alkoxy carbonyl or phenoxy carbonyl; acyl group, alkoxy carbonyl group or phenoxy carbonyl group; provided that R^1 and R^2 or R^1 and R^3 may combine with each other to form a ring, or R^1 , R^2 and R^3 may combine altogether to form a condensed ring, which comprises reacting an olefin represented by the formula (1)



wherein R^1 , R^2 , R^3 and R^4 are the same as defined above, with oxygen in the presence of an aldehyde.

2. A process for producing an epoxide represented by the formula (2) which comprises reacting an olefin represented by the formula (1) with oxygen in the presence of an aldehyde, in the presence or absence of a proton source and in the presence of an iron – containing catalyst or a copper – containing catalyst.

3. The process according to Claim 1, wherein the aldehyde is 2-methylpropanal, 2-methylbutanal, isovaleraldehyde or pivalaldehyde.
4. The process according to Claim 2, wherein the iron-containing catalyst is Fe, $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot n\text{H}_2\text{O}$, $\text{Fe}(\text{OAc})_3$ or Fe_2O_3 .
5. The process according to Claim 2, wherein the iron-containing catalyst is Fe or Fe_2O_3 .
6. The process according to Claim 2, wherein the copper-containing catalyst is Cu, CuCl, $\text{Cu}(\text{OAc})_2 \cdot n\text{H}_2\text{O}$, $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OCH}_3)_2$, Cu_2O or CuO.
7. The process according to Claim 2, wherein the copper-containing catalyst is Cu, $\text{Cu}(\text{OH})_2$, Cu_2O or CuO.
8. The process according to Claim 2, wherein the proton source is acetic acid or benzoic acid.
9. The process according to Claim 2, wherein the amount of proton source is 1 – 100 moles per mole of the iron-containing or copper-containing catalyst.
10. The process according to Claim 1 or 2, wherein the amount of the aldehyde is 1 – 30 moles per mole of the olefin.
11. The process according to Claim 1 or 2, wherein the amount of the catalyst is 0.01 – 120% by mole relative to the olefin.
12. The process according to Claim 1 or 2, wherein the reaction is performed in a solvent.
13. The process according to Claim 12, wherein the solvent is dichloromethane, ethyl acetate, acetonitrile or benzene.
14. The process according to Claim 1 or 2, wherein the reaction temperature is 0°C to the reflux temperature of the reaction mixture.
15. The process according to Claim 1 or 2, wherein the reaction time is 1 to 48 hours.
16. The process according to Claim 1 or 2, wherein the oxygen is supplied by blowing it into the reaction system.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 8554

Page 1

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FR-A-1 594 466 (BASF AKTIENGESELLSCHAFT) * the whole document, particularly page 2, lines 1-3, page 3, lines 11, 12 and examples 1-3 * ---	1,3,10, 12-16	C07D301/06 C07D303/02
X	FR-A-1 367 771 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) * the whole document, particularly page 2, left-hand column, paragraph 4 and examples 2 and 3 * ---	1-16	
X	FR-A-1 323 787 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) * the whole document, particularly example 11 and page 7, table VI, runs 3 and 7 * ---	1-16	
X	FR-A-1 377 981 (SHAWINIGAN CHEMICALS LIMITED) * the whole document, particularly examples 10 and 11 * ---	1-16	
X	FR-A-1 400 305 (EASTMAN KODAK COMPANY) * the whole document * ---	1,3,10, 12-16	C07D
X	FR-A-2 073 743 (UNION CARBIDE CORPORATION) * the whole document * ---	1,3,10, 12-16	
X	DE-A-1 937 387 (BASF AKTIENGESELLSCHAFT) * the whole document, particularly the examples * ---	1,3,10, 12-16	
X	DE-A-1 568 407 (DEUTSCHE AKADEMIE DER WISSENSCHAFTEN ZU BERLIN) * the whole document * ---	1,3,10, 12-16	
		-/--	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 04 FEBRUARY 1993	Examiner ALLARD M.S.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 8554
Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FR-A-1 376 471 (INSTITUT FRANÇAIS DU PÉTROLE, DES CARBURANTS ET LUBRIFIANTS) * the whole document * ---	1-16	
X	BE-A-682 335 (IMPERIAL CHEMICAL INDUSTRIES LIMITED) * thw whole document, particularly examples 1 and 3 * -----	1-16	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 04 FEBRUARY 1993	Examiner ALLARD M.S.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			